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(19) (CA) **CANADIAN PATENT** (12)

(54) Storage-Stable Anionic Liquid Detergent Compositions
Containing Amphoteric Distyryl Derivatives

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Storage-stable anionic liquid detergent compositions containing
amphoteric distyryl derivatives

Abstract of the Disclosure

Storage-stable anionic liquid detergent compositions containing fluorescent whitening agents of the class of the amphoteric distyryls. These detergent compositions cause no bleach spots when they come in contact with textile fabric.

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Storage-stable anionic liquid detergent compositions containing
amphoteric distyryl derivatives

The present invention relates to storage-stable anionic liquid detergents which contain amphoteric distyryl derivatives as fluorescent whitening agents.

It is known to use fluorescent whitening agents in liquid detergents. During the treatment they exhaust on to the material to be washed and, by virtue of their special light absorption/emission property, result in elimination of the yellowish hues and in an enhancement of the degree of whiteness.

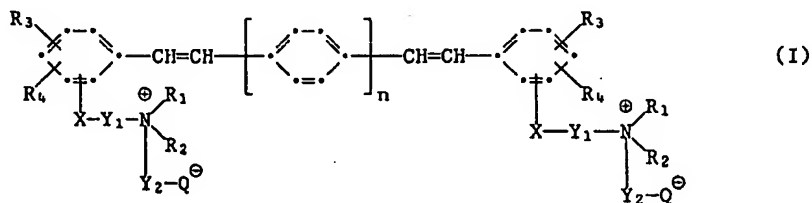
However, this effect is also responsible for the appearance of bleach spots if textile fabric comes into direct contact with the liquid detergent, for example in a pretreatment. For this reason, European patent application 167 205 proposes the use of monosulfonated stilbene-triazolyl, triazine or distyrylbiphenyl whitening agents in anionic liquid detergents as a solution to this problem.

It is also known to use amphoteric fluorescent whitening agents in cationic liquid detergent compositions (q.v. European patent application 59 684). The use of amphoteric fluorescent whitening agents in anionic liquid detergent compositions has so far not been disclosed.

Surprisingly, it has been found that amphoteric distyryl fluorescent whitening agents can also be incorporated in anionic liquid detergents, and that it is thereby possible to prevent the formation of bleach spots and at the same time to impart excellent white effects and detergent stability.



Accordingly, the present invention relates to anionic liquid detergent compositions containing 0.01 to 2 % of fluorescent whitening agent consisting of an amphoteric distyryl compound, or a mixture of distyryl compounds, of formula I



wherein

X is oxygen, sulfur, a direct bond, $-\text{SO}_2\text{N}(\text{R}_5)-$, $-\text{CON}(\text{R}_5)-$ or $-\text{COO}-$,

Y₁ and Y₂ are each independently of the other C₁-C₄alkylene or hydroxy-propylene,

R₁ and R₂ are each independently of the other C₁-C₄alkyl or $-\text{NR}_1\text{R}_2$ is a pyrrolidine, piperidine, hexamethylenimine or morpholine ring, and R₁ together with R₅ is also a piperazine ring,

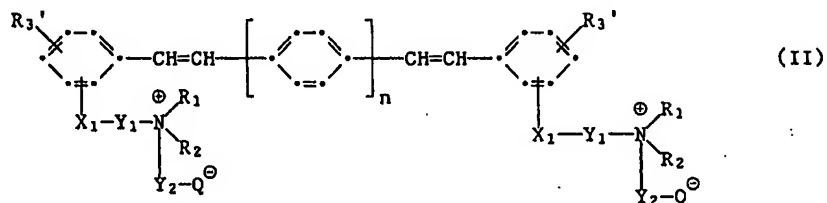
R₃ and R₄ are each independently of the other hydrogen, C₁-C₄alkyl, halogen, C₁-C₄alkoxy, C₃-C₄alkenyl, $-\text{CN}$ or, in ortho-position to each other, together are a trimethylene or tetramethylene group.

R₅ is hydrogen, C₁-C₄alkyl, cyanoethyl or, together with R₁, is a piperazine ring,

Q is $-\text{COO}$ or $-\text{SO}_3$, and

n is 1 or 2.

It is preferred to use amphoteric distyryl derivatives of formula II

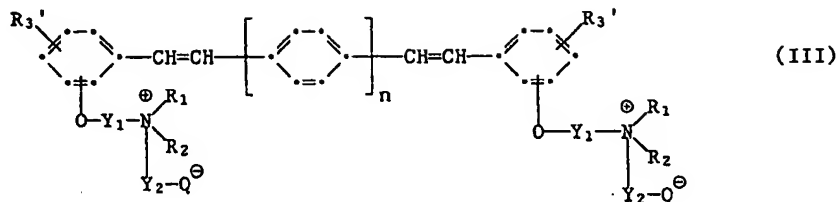


wherein R₁, R₂, Y₁, Y₂, Q and n are as defined above, and

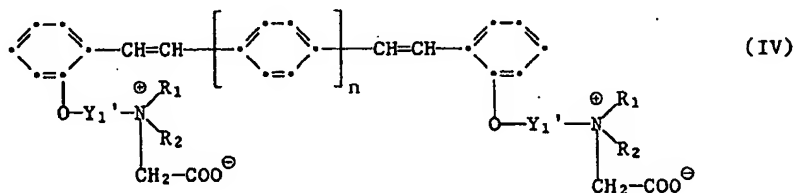
X₁ is oxygen, a direct bond, $-\text{CONH}-$ or $-\text{COO}-$, and

R₃' is hydrogen, C₁-C₄alkyl, methoxy or chloro.

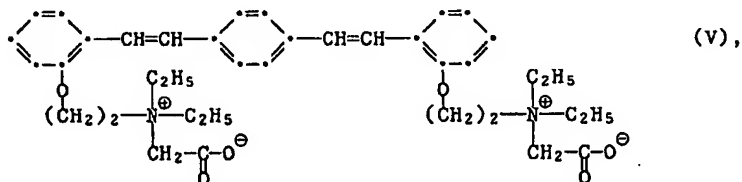
It is especially preferred to use amphoteric distyryl derivatives of formula III



wherein R_1 , R_2 , R_3 , Y_1 , Y_2 , Q and n are as defined above; and, first and foremost, the amphoteric distyryl derivatives of formula IV



wherein Y_1 is C_1 - C_4 alkylene and R_1 , R_2 and n are as defined above, for example the compound of formula V



The amphoteric distyryl derivatives of formulae I to V are known and can be prepared by known methods (q.v. for example European patent application 59 684).

The term anionic liquid detergent compositions will be understood as meaning the known and commercially available detergent compositions of general anionic character described, for example, in European patent application 167 205 or US patent 4 507 219.

In addition to the above amphoteric styryl derivatives, the liquid detergents preferably contain 1 to 60 % of anionic, non-ionic, zwitter-ionic and, in some cases, small amounts of cationic surfactants and 25 to 65 %, preferably 40 to 55 %, of water. Specifically, the detergent composition contains, in addition to the fluorescent whitening agent, 3 to 50 %, preferably 15 to 25 %, of anionic surfactants, 2 to 30 %, preferably 4 to 15 %, of non-ionic surfactants, 3 to 30 %, preferably 5 to 20 %, of ethoxylated or non-ethoxylated (C₁₀-C₂₂) fatty acids, especially saturated (C₁₀-C₁₄) fatty acids such as capric, lauric, myristic, coconut and palm kernel fatty acid and mixtures thereof, 1 to 25 %, preferably 1 to 10 %, of builders and, if appropriate, 1 to 10 %, preferably 1 to 5 %, of zwitterionic surfactants, 0.5 to 3 %, preferably 0.7 to 2 %, of quaternary ammonium, amine or amine oxide surfactants and 1 to 10 % of conventional detergent additives such as enzymes, enzyme stabilizers, antioxidants, preservatives and disinfectants, fragrances and dyes, complexing agents and/or sequestering agents and solvents.

Useful surfactants are described, for example, in US patents 4 285 841, 3 929 678 and 4 284 532 and British patent 2 041 986. Anionic surfactants which may suitably be used are, for example, water-soluble salts of organic sulfur compounds which contain alkyl and/or aryl groups, sulfonic acids or sulfonic acid esters containing 10 to 20 carbon atoms in the alkyl moiety, for example alkyl sulfates, preferably those obtained by sulfation of higher (C₁₀-C₁₈) alcohols, linear or branched alkylbenzenesulfonates containing 9 to 15 carbon atoms in the alkyl moieties, preferably linear alkylbenzenesulfonates containing 11 to 14 carbon atoms in the alkyl moieties, alkanesulfonates of 8 to 24, preferably 12 to 18 carbon atoms, alkyl glyceryl ether sulfonates of 8 to 18 carbon atoms, alkyl phenol ethylene oxide ether sulfates containing 1 to 4 mol of ethylene oxide per molecule and 8 to 12 carbon atoms in the alkyl moieties, alkyl ethylene oxide ether sulfates containing 1 to 4 mol of ethylene oxide per molecule and 10 to 20 carbon atoms in the alkyl moieties, water-soluble salts or esters of a α -sulfonated fatty acids containing 6 to 20 carbon atoms in the fatty acid and 1 to 10 carbon atoms in the ester group, water-soluble salts of 2-acyloxyalkane-1-sulfonic acid containing 2 to 9 carbon atoms in the acyl group and 9 to

23 carbon atoms in the alkane moiety, water-soluble salts of olefin sulfonates of 12 to 24 carbon atoms and β -alkoxyalkanesulfonates containing 1 to 3 carbon atoms in the alkyl moieties and 8 to 20 carbon atoms in the alkane moiety. Non-ionic surfactants which may suitably be used are, for example, ethoxylated non-ionic compounds of formula $R'(OC_2H_4)_nOH$, wherein R' is an alkyl group of 10 to 16 carbon atoms or an alkylphenyl group containing 8 to 12 carbon atoms in the alkyl moiety, n is an integer from 3 to 9, which surfactants have a HLB (hydrophilic-lipophilic balance) of 10 to 13. The surfactants employed are in particular those cited as preferred in EP-A-167 205. The most eligible anionic surfactants, however, are ethoxylated or non-ethoxylated C_{10} - C_{18} alkylsulfates, e.g. in the form of the triethanolamine salts, C_{10} - C_{18} alkylbenzenesulfonates or mixtures thereof, and non-ionic surfactants which are preferably used are condensation products of one mol of (C_{10} - C_{15}) fatty alcohol with 3 to 8 mol of ethylene oxide.

Suitable builders are the polycarboxylates cited in US patents 4 321 165 and 4 284 532, for example water-soluble aminopolycarboxylates, cycloalkanepolycarboxylates, ether polycarboxylates, alkylpolycarboxylates, epoxy polycarboxylates, tetrahydrofuran polycarboxylates, benzenepolycarboxylates and polyacetyl polycarboxylates, preferably the sodium and potassium salts of ethylenediaminetetraacetate, nitrilotriacetate and phytic acid, water-soluble polymers and copolymers of itaconic acid, aconitic acid, maleic acid, fumaric acid, mesaconic acid, methylmalonic acid and citraconic acid, as well as the sodium and potassium salts of mellitic acid, pyromellitic acid, benzenepentacarboxylic acid, oxydiacetic acid, carboxymethoxysuccinic acid, carboxymethoxymalonic acid, cis-cyclohexanehexacarboxylic acid, cis-cyclopentanetettracarboxylic acid, oxydisuccinic acid and, most preferably, citric acid and citrates.

The liquid detergent compositions are prepared by simple mixing of the individual components and are used for washing and pretreating textile fabrics.

The liquid detergent compositions of this invention are stable for several months and cause no bleach spots when they come in contact with textile fabrics.

The following Examples will serve to illustrate the invention. Parts and percentages are by weight. The spotting test is carried out in the following manner:

Spotting test

a) Whitening agent/detergent formulation:

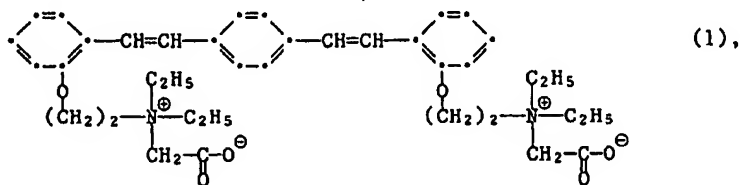
0.1 % (100 % of active substance) of fluorescent whitening agent or mixture of fluorescent whitening agents is dissolved in a liquid detergent. 0.6 g of this detergent solution (A) is diluted with 400 ml of water (10°-12° dH) at a temperature of 30°C (detergent solution B).

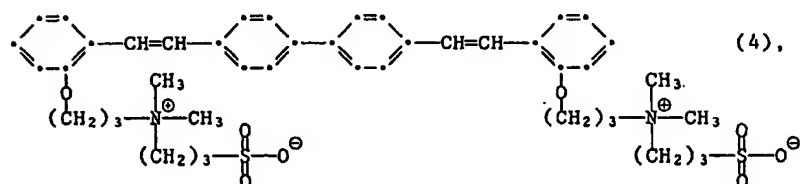
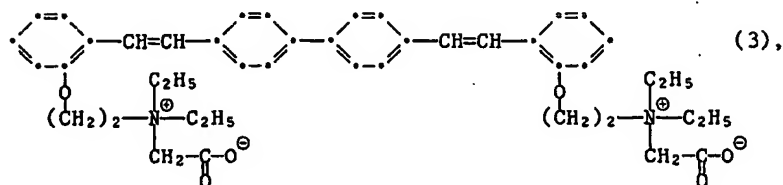
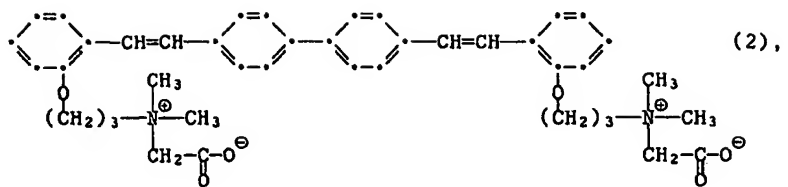
b) A piece of bleached cotton fabric (20 g) is clamped on a stenter frame.

c) 0.6 ml of detergent solution (A) is applied uniformly with a pipette to a premarked round area (5 cm diameter) of this cotton fabric which, after a treatment time of 30 seconds, is put into the prepared detergent solution (B) and washed for 15 minutes at 30°C. The cotton fabric is then rinsed with cold water and dried at 70°C.

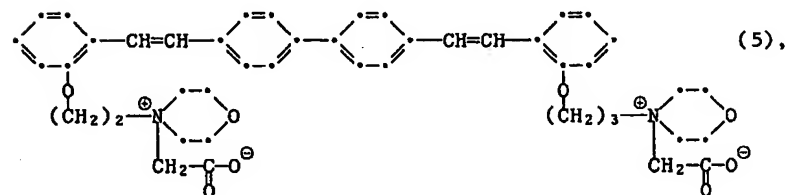
d) The difference in the degree of whiteness according to Ganz between the treated area and the surrounding area is a criterion of the so-called spotting behaviour (formation of bleach spots) and is determined by inspecting the textile fabric.

Example 1: A bleached cotton fabric is washed at a liquor to goods ratio of 1:20 for 15 minutes in a warm aqueous liquor of 60°C that contains, per litre, 3 g of one of the following liquid detergent solutions a), b) or c) and 0.1 % of a fluorescent whitening agent of formula





or



based on said detergent solution. The cotton fabric is then rinsed for 20 seconds in running water and dried at 70°C in a drying oven. The treated fabric exhibits an excellent white effect even after repeating the washing procedure 5 to 10 times.

The liquid detergent employed is prepared by mixing the following components (% by weight):

- a) 15 % of C₁₁-C₁₃alkylbenzenesulfonate
- 14 % of C₁₄-C₁₅fatty alcohol polyethoxylate (ethylene oxide 7)
- 10 % of soap flakes
- 9 % of ethanol

4 % of sodium citrate
5 % of triethanolamine
43 % of water.

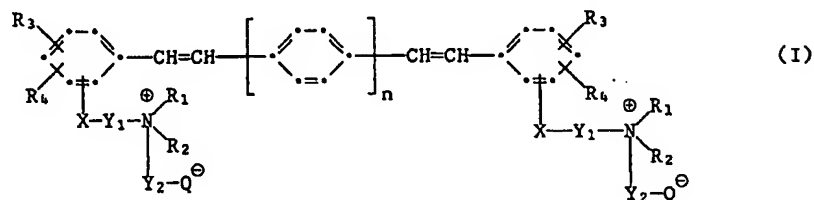
b) 7.5 % of C₁₃alkylbenzenesulfonate
12 % of C₁₄-C₁₅alkylpolyethoxysulfonate (ethylene oxide 2.25)
15 % of C₁₁-C₁₃fatty acid potassium salt
10 % of C₁₂-C₁₃fatty alcohol polyethoxylate (ethylene oxide 8)
5.5 % of sodium citrate
12 % of a 1:1 mixture of isopropyl alcohol and ethanol
0.7 % of C₁₂alkyltrimethylammonium chloride
37.3 % of water.

c) 11.5 % of C₁₁-C₁₃alkylbenzenesulfonate
3.8 % of triethanolamine lauryl sulfonate
15.5 % of potassium soap
15 % of C₁₁-C₁₃fatty alcohol polyethoxylate (ethylene oxide 7)
5 % of triethanolamine
10 % of ethanol
39.2 % of water.

Example 2: The spotting test is carried out with compounds of formulae 1-5 and the respective liquid detergent composition a), b) or c). All compounds are stable for several months in the three detergent compositions, have good whitening properties, and induce no, or only insignificant, spotting.

What is claimed is:

1. An anionic liquid detergent composition containing 0.01 to 2 % of fluorescent whitening agent consisting of an amphoteric distyryl compound, or a mixture of distyryl compounds, of formula I



wherein

X is oxygen, sulfur, a direct bond, $-\text{SO}_2\text{N}(\text{R}_5)-$, $-\text{CON}(\text{R}_5)-$ or $-\text{COO}-$,

Y₁ and Y₂ are each independently of the other C₁-C₄alkylene or hydroxypropylene,

R₁ and R₂ are each independently of the other C₁-C₄alkyl or $-\text{NR}_1\text{R}_2$ is a pyrrolidine, piperidine, hexamethylenimine or morpholine ring, and R₁ together with R₅ is also a piperazine ring,

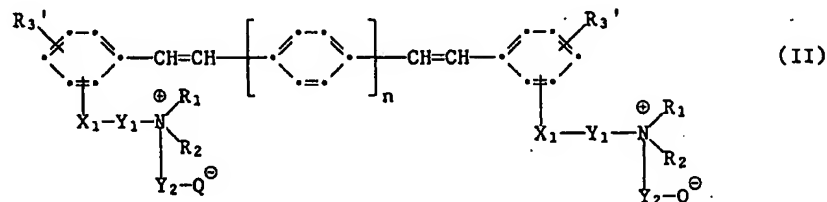
R₃ and R₄ are each independently of the other hydrogen, C₁-C₄alkyl, halogen, C₁-C₄alkoxy, C₃-C₄alkenyl, $-\text{CN}$ or, in ortho-position to each other, together are a trimethylene or tetramethylene group.

R₅ is hydrogen, C₁-C₄alkyl, cyanoethyl or, together with R₁, is a piperazine ring,

Q is $-\text{COO}$ or $-\text{SO}_3$, and

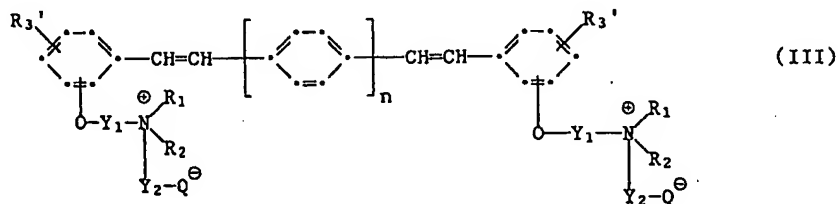
n is 1 or 2.

2. An anionic liquid detergent composition according to claim 1, which contains amphoteric distyryl fluorescent whitening agents of formula II



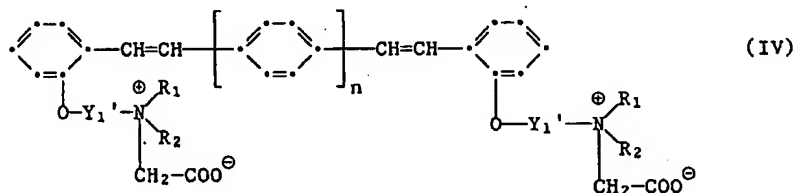
wherein R_1 , R_2 , Y_1 , Y_2 , Q and n are as defined above, and
 X_1 is oxygen, a direct bond, $-\text{CONH}-$ or $-\text{COO}-$, and
 R_3 is hydrogen, $\text{C}_1\text{-C}_4$ alkyl, methoxy or chloro.

3. An anionic liquid detergent composition according to claim 2, which contains amphoteric distyryl fluorescent whitening agents of formula III



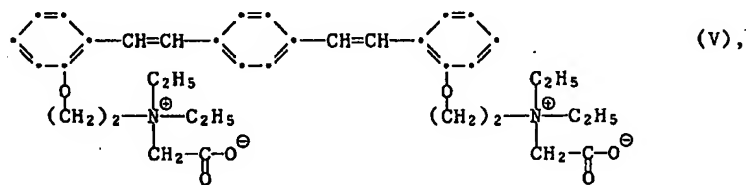
wherein R_1 , R_2 , R_3 , Y_1 , Y_2 , Q and n are as defined in claim 2.

4. An anionic liquid detergent composition according to claim 2, which contains amphoteric distyryl fluorescent whitening agents of formula IV

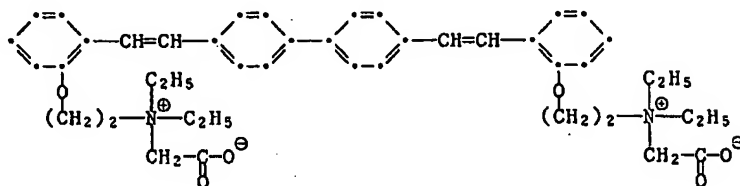


wherein Y_1 is $\text{C}_1\text{-C}_4$ alkylene and R_1 , R_2 and n are as defined in claim 2.

5. An anionic liquid detergent composition according to claim 2, which contains a distyryl fluorescent whitening agent of formula V



6. An anionic liquid detergent composition according to claim 2, which contains a distyryl fluorescent whitening agent of formula



7. A process for washing and pretreating textile fabrics, which comprises the use of an anionic liquid detergent composition as claimed in claim 1.

8. A process for the preparation of an anionic liquid detergent composition as claimed in claim 1 by simple mixing of the individual components.

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